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(54) ARTICLES FOR ABSORBING LIQUID BODY DISCHARGES AND MATERIALS THEREFOR

(71) We, CELANESE CORPORATION, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to diapers, sanitary napkins and other articles for absorbing liquid body discharges and to materials for use in their manufacture.

Because of the cost and unpleasant nature of the task of cleaning cloth diapers various types of disposable diapers intended to be discarded after use have been put on the market. There are also other articles, e.g. sanitary napkins and tampons, used for absorbing liquid body discharges which are discarded after a single use. The ready disposal of all such articles presents a problem for which the present invention provides an acceptable solution by providing articles of the type referred to which can be disposed of in the domestic toilet bowl and flushed away without danger of causing clogging of the waste pipes of the sewage system.

According to the invention a disposable article or material for absorbing liquid body discharges comprises an absorbent water dispersible fibrous pad covered on at least one side with a liquid permeable bonded fibre covering comprising biodegradable fibres held together by a water insoluble organic polymer which is non-irritating to the human body, stable when in contact with such a body discharge and has a D value (as hereinafter defined) no greater than 5, a one-inch wide strip of said covering being able to sustain a pull of at least 2.0 pounds when dry and a pull of at least 0.25 pounds when wet and capable of elongation without rupture by from 3 to 50% of its length whether wet or dry.

The articles and materials of the invention readily disintegrate in water rendered either more strongly acid or more strongly alkaline, according to the particular water insoluble polymer used, than liquid body discharges the speed with which this occurs depending on the D value of the polymer used. In this Specification the D value of a polymer is the time taken for it to become sufficiently solubilized in the more strongly acidic or alkaline medium for the covering to break up, so as to release the fibres of the pad, when that time is determined as follows:

A bonded fibre covering is made from cellulosic fibres which are less than half an inch long bonded with a proportion of the polymer amounting to 30% of the total weight of fibre and polymer. A strip of the covering two inches long and one inch wide is heated to 90°C. for approximately ten minutes and then placed in a litre of water at room temperature (15° to 25°C.) to which 2 cc of either 1.0 Normal hydrochloric acid or 1.0 Normal caustic soda has been added according to whether the polymer is one which is sufficiently solubilized by an acid or an alkaline medium respectively. The material is stirred in the solution until it disintegrates and the time taken for this result to be achieved is the D value of the polymer. It is preferred to use a polymer having a D value no greater than 3. As stated above the polymer used to hold together the fibres of the covering must be unaffected by contact with body discharges during use and obviously, this excludes all water soluble polymers. As a matter of fact, body discharges broadly range in pH between extremes of approximately 4.6 and 8.4 so that the polymers must be stable in such slightly alkaline and slightly acidic discharges encountered during use. Quite obviously, the exact pH encountered within the broad range set forth varies depending upon many factors including the specific end use. Thus, diapers and sanitary napkins are not necessarily subjected to the same pH ranges during use. Therefore, the polymers employed need to be stable only in the particular body discharge encountered during use.

[*Price 5s. 0d. (25p)*]

Price 33p

It is to be noted, however, that water soluble polymers can be initially used for application to the biodegradable fibres from aqueous solutions of the polymer providing such polymers are subsequently treated to ensure that the polymer in the finished product is water insoluble.

The polymers must not develop irreversible crosslinking either in the manufacture of the disposable products or in the use thereof. some of the bonding polymers used in making bonded fibre products are subjected to chemical treatment or significantly high temperatures so that they became irreversibly crosslinked. Although this technique does improve the bond between biodegradable fibres such as cellulosic fibres and the polymer, it does not result in the production of products which readily disintegrate in aqueous acidic or alkaline media. It is to be understood, however, that polymers which are only temporarily or reversibly crosslinked can be used. Thus, for example, a polymer can be reacted with a metal salt so that it crosslinks by ionic crosslinking to form a product which, when treated with a base, loses the crosslinking and is solubilized.

Another important characteristic of the polymers employed is that they be non-irritating to the human body and when combined with cellulose fibres the resulting product should possess a pleasing feel to the hand.

In this connection, a test method has been devised to determine whether or not a candidate polymer is non-irritating to the human skin. In this test a sample, one inch square, of the covering made with the polymer is applied to the skin and held in place with adhesive tape. After 48 hours the sample is removed and 10 to 14 days allowed to elapse. The test is then repeated for an additional 48 hours. If any redness, scaliness, accumulation of fluid in the skin or other signs of irritation are apparent the polymer is considered unsuitable. This test is more fully described in The (United States of America) Public Health Report, Vol. 59, 1944 under Prophetic Patch Test at page 551.

Thus, the expression "non-irritating to the human skin" as used in this Specification defines a polymer which satisfies the above test procedure.

The products of the invention need such dry strength that handling, folding or packaging will not tear or puncture them and, to this end, a one-inch wide strip of the covering must be able to sustain a pull of at least 2.0 pounds; such a product is hereinafter described as having a dry break strength of at least 2.0 pounds. Moreover, for the products to posses sufficient wet strength to maintain their structural integrity under conditions of use, a one inch wide strip of the covering must be able when wet to sustain a pull of at least 0.25 and preferably, at least 0.5 pounds; such a product is hereinafter described as having a wet strength of 0.25 (or 0.5) pounds. The wet and dry strengths are not sufficient to characterize a satisfactory product in view of the fact that the degree of stretch must also be taken into consideration if these products are to function properly and it has been found that the products must be capable of elongation without rupture of from 3 to 50 percent whether wet or dry.

The above figures are those obtained by the use of a conventional Instron Testing Machine using six inch lengths of the one-inch wide strip which have been kept at 73.4°F. and 50% relative humidity for 48 hours. The strip is then inserted into the rubber-faced jaws of the Instron Testing Machine to a gauge length of two inches and tested at an elongation rate of four inches per minute.

In determining the wet strength and wet elongation the sample strip is soaked in water having a pH of 7 for 10 minutes after the 48-hour treatment previously referred to and thereafter tested.

The biodegradable fibres in the bonded fibre covering may be protein fibres, e.g. silk or wool, although cellulosic fibres are preferred, e.g. rayon staple fibre, wood pulp of moderate alpha cellulose content and cotton linters. The average fibre length is not narrowly critical and any convenient length can be employed, although it is advantageous to use fibres less than half an inch and, especially, less than a quarter inch long.

Polymers which are stable in neutral or acidic media but which exhibit satisfactory D values in alkaline media are various copolymers of ethylenically unsaturated mono and polycarboxylic acids with ethylenically unsaturated esters or nitriles, e.g. copolymers of acrylic or methacrylic acid with an alkyl acrylate or methacrylate, e.g. ethyl acrylate or methyl methacrylate, or with acrylonitrile; carboxy ester lactones; copolymers of alpha, beta, ethylenically unsaturated dicarboxylic acids, e.g. maleic acid, with vinyl compounds such as styrene; polyacrylic acid-polyether addition products, stytene-monoethyl maleate heteropolymers and itaconic acid polymers.

Polymers which are stable in neutral or alkaline media but which exhibit satisfactory D values in acidic media include various copolymers of aminoacrylates, e.g. dimethylaminomethacrylate, with alkyl acrylates, e.g. ethyl acrylate and also polyvinylpyridines.

Specific polymers possessing all the properties needed to yield a satisfactory product, including D values less than 5 in 1.0 Normal caustic soda, include a copolymer of 80 parts by weight ethylacrylate and 20 parts by weight methacrylic acid, a copolymer comprising 60 parts by weight of acrylonitrile

and 40 parts by weight methacrylic acid, and the butyl half ester of a copolymer of methyl vinyl ether and maleic anhydride.

The polymer can, most conveniently, be sprayed as a solution on to a preformed web of the biodegradable fibres but it can also be applied by passing such a web through nip rolls which are wet with a solution of the polymer. The wet web can then be dried in hot air. The polymer can also be added during a pulp beating operation such as is used in paper making. This method, however, is more wasteful of polymer since a significant amount will be lost in drainage.

A suitable fibrous web may be formed, for instance, by carding, garneting, or by dry deposition from air suspension of the fibres and, after being impregnated with a solution or dispersion of the polymer, oven dried at temperatures sufficiently low to prevent the polymer from becoming thermally cross-linked, i.e. below 150°C., and preferably, at temperatures of from 70° to 120°C.

The amount of polymer employed is carefully controlled since too little will not yield a product of sufficient strength whereas too much will result in a product with too high a D value. It has been found that suitable products are usually obtained when cellulosic fibres are held together with sufficient polymer for it to form 10 to 60 weight percent of the final bonded fibre covering.

The absorbent fibrous pad to which the covering is applied can be composed of, for instance, foamed cellulose, shredded wood pulp or cotton linters, and, in a preferred embodiment of the invention, shredded wood pulp in the form of a batt as produced, for example, by a Rando-Webber machine (Curlator Company, Rochester, New York, United States of America), is used. Foamed material suitable for use as the absorbent pad can be prepared simply by agitating a mixture of short length fibres and a wetting agent in water to produce a foamed material and drying the foamed material. The average fibre length is advantageously less than half an inch, and desirably less than a quarter inch. In preparing the foamed material, the fibrous cellulosic material and water are generally used in a weight ratio of water to cellulose of at least 10 : 1; cellulose must form at least 0.7% by weight of the total foamed slurry for satisfactory results. Preferred wetting agents are the anionic surfactants such as the salts of long-chain sulphites and sulphates, e.g. the sodium sulphate derivative of 3,9-diethyl tridecanol-6, the ammonium sulphate ester of alkylphenoxypoly(ethyl-enoxy)ethanol and the coconut oil acid ester of sodium isethionate. The proportion of foaming agent is advantageously in the range of 0.2 to 1% by weight based on the weight of water in the slurry.

The bonded fibre covering can be used to cover both sides of the absorbent fibrous pad but, in one embodiment of the invention, one side of the pad is covered by a moisture impermeable film composed of a material which has water solubility properties similar to those of the polymer employed in the covering; the film can in fact be one which is cast from the same polymer.

The products of the invention, after use, can be disposed of simply by being placed in a toilet bowl to which is added a suitable acidic or alkaline agent according to the nature of the polymer used to hold together the fibres of the covering. Typical examples of alkaline materials include ammonia, sodium carbonates, ammonium borate, alkali metal borates, phosphates and silicates, e.g. soidum borate, potassium phosphate or potassium silicate and sodium hypochlorite. Typical acidic substances are citric acid, boric acid and acid salts such as calcium and ammonium chloride. Obviously, any acid or base can be employed, e.g. dilute hydrochloric acid or dilute potassium hydroxide, but these materials would not generally be found in the home.

It is to be noted that the acid or alkaline agent, *per se*, does not disperse the products since it only interacts with the polymer and the biodegradable fibres are dispersed only upon agitation. While this can be accomplished by stirring it is achieved more simply by the act of flushing the toilet.

Perfumes, deodorants, dyes, bacteriostatic agents or other modifying substances can be incorporated into the products, *per se*, either in the covering or in the absorbent pad or in both or into prepacked quantities of acidic or alkaline substances supplied for use with the products of the invention.

The following Examples illustrate the invention.

Example 1

60 grams of acrylonitrile and 40 grams of methacrylic acid are mixed together to form a monomer mixture. Four hundred grams of acetonitrile are heated to reflux. One half gram of benzoylperoxide dissolved in acetonitrile is added to the refluxing acetonitrile and the monomer mixture is added over a period of one hour. An additional one half gram of benzoyl peroxide is added and reflux is continued for three hours. The precipitated polymer is recovered, and washed free of acetonitrile.

The precipitated polymer is found to be non-irritating to the human skin. It is found to be substantially free from any crosslinking.

A portion of the above polymer was

dissolved in toluene and applied to a web of cellulose fibres by impregnation and the web was then dried in air at a temperature of about 100°C to yield a composition comprising 70 parts by weight of cellulose fibres to 30 parts by weight of the above polymer.

A sample strip two inches long and one inch wide was tested for its degradability value (D) in accordance with the procedure set forth above and it was found to have a D value of approximately 2.

A strip 14 inches long by $4^1/_2$ inches wide was cut from said web and used to cover 20 grams of a non-woven absorbent pad of cellulose fibres to form a diaper. The diaper cover was found to possess the following physical characteristics.

Dry break strength	9·5 pounds
Wet strength	2·6 pounds
Dry elongation	3·8 percent
Wet elongation	10·3 percent

The above diaper was found to be stable when in contact with body discharges. However, if after use it is placed in a toilet and two grams of sodium hydroxide are added, it is found that after about 3 minutes the polymer is degraded so that the diaper disintegrated and could be safely flushed.

Example 2

Alkali Soluble Polymer

2400 grams of benzene were placed in a reactor and heated to 80°C 3 grams of benzoyl peroxide was added to the reactor and the solution was swept with nitrogen. A solution of 90 grams of styrene, 180 grams of methacrylic acid, 330 grams of 2-ethylhexyl acrylate, and 3 grams of benzoyl peroxide was added to the reactor held at 80°C over a period of 30 minutes. After one hour at 80°C, 3′ grams of benzoyl peroxide was added to the reactor and heating was continued at 80°C for two hours. The heating of the reactor was then stopped and the reaction was left to cool to room temperature. One to two liters of acetone was added to the cooled reactor and the precipitated polymer was filtered and dried. The dried polymer was dissolved in dioxane and applied to a cellulose fibre web to make a covering for diapers and sanitary napkins. The product was found to be non-irritating to the human skin and to have a D value of 2. The product had the following physical properties.

Dry break strength	6·4 pounds
Wet break strength	0·8 pounds
Dry elongation	5·6 percent
Wet elongation	7·8 percent

Example 3

Acid Soluble Polymer

20 grams of ammonium persulfate were dissolved in 50 ml of water. 11 grams of sodium meta bisulfite was dissolved in 50 ml of water. These solutions were the initiators used in the polymerization described below.

396 grams of water, 3 grams of Alipal CO-436, 9.8 grams of Igepal CO-977, and 25 grams of Igepal CO-897 were added to the reactor, and nitrogen gas was bubbled through the solution for 15 minutes at 50°C reactor temperature. 10 ml each of the initiator solutions were added to the reactor and a comonomer solution of 293.4 grams of ethylacrylate and 72.8 grams of dimethylaminoethyl methacrylate was added to reactor at 40°C over a two-hour period. The remainder of the initiator solutions was also added to the reactor over a period of two hours. After all the reactants were added, the polymerization reaction was held at approximately 40°C for $^1/_2$ hour. The emulsion polymer formed can be used to bond together the fibres of a cellulose web to form a covering of satisfactory wet and dry strengths and elongations which disintegrates in acidic media; the polymer has a D value of 3.

Example 4

350 grams of water and 15 grams of Alipal CO-436 (alkylphenol-ethylene oxide condensation product) were placed in a reactor and heated to 55°C under a nitrogen gas sweep. A monomer mixture was prepared from 75 grams of methacrylic acid, 75 grams of acrylonitrile, 150 grams of water, 0.3 grams of hydroxyethyl cellulose, and 15 grams of Alipal CO-436 and 150 grams of 2-ethyl hexoacrylate were mixed in a Waring Blender for one minute. 25 percent by volume of this mixture was added to the reactor at 55°C together with 25 percent by volume of separate initiator solutions prepared by dissolving 1.8 grams of ammonium persulfate and 0.9 grams of sodium metabisulfite respectively in 60 ml of water. The remainder of the monomer mixture was then added over a 15-minute period and the remainder of each initiator solution was also added over a 30-minute period. The reactor was maintained at about 55°C for four hours to yield an emulsion polymer.

A web of cellulose fibers was impregnated with the above polymer emulsion and dried to form a covering containing 30% by weight of the polymer. The covering was used to cover an absorbent pad of unbound cellulosic fibers in order to make sanitary products such as diapers and sanitary napkins.

The covering of the sanitary products had the following properties:

Dry break strength	9·4 pounds
Wet break strength	1·6 pounds
Dry elongation	6·5 percent
Wet elongation	8·8 percent
D value (1·0 N caustic soda)	3

Example 5

The procedure of Example 2 was repeated with the exception that 15 parts by weight of styrene, 30 parts by weight of methacrylic acid and 55 parts by weight of 2-ethylhexylacrylate were employed.

When this polymer was used to bond cellulosic fibers, a covering was obtained which had a D value of 1 and adequate dry and wet strengths and elongations for it to be used in the preparation of sanitary products, by using the same to cover a padding of unbound cellulosic fibers, which disintegrate in alkaline media.

Example 6

In a manner analogous to the procedure described in Example 2, a polymer was prepared by polymerizing a monomer mixture comprising 20 parts by weight of methyl methacrylate, 55 parts by weight of 2-ethylhexylacrylate and 25 parts by weight of methacrylic acid.

When this polymer was used to bond a web of cellulosic fibres, a product was obtained which possessed excellent physical properties and was suitable for use in the preparation of sanitary products by using the same to cover a pad of unbound cellulosic fibres. The polymer had a D value of one in 1.0 Normal caustic soda.

Example 7

The procedure of Example 1 was repeated with the exception that 75 parts by weight of methacrylamide were employed instead of the acrylonitrile and 25 parts by weight of methacrylic acid were also used.

The resulting polymer, which had a D value of 3 in 1.0 Normal caustic soda, was used as a binder for cellulosic fibres to form a covering containing 24% by weight of the polymer. The product obtained possessed the following physical properties:

Dry break strength	5·6 pounds
Wet break strength	0·52 pounds

and adequate dry and wet elongation for it to be used to cover absorbent sanitary products.

WHAT WE CLAIM IS:—

1. A disposable article or material for absorbing liquid body discharges, which comprises an absorbent water dispersible fibrous pad covered on at least one side with a liquid permeable bonded fibre covering comprising biodegradable fibres held together by a water insoluble organic polymer which is non-irritating to the human body, stable when in contact with such a body discharge and has a D value (as hereinbefore defined) no greater than 5, a one-inch wide strip of said covering being able to sustain a pull of at least 2.0 pounds when dry and a pull of at least 0.25 pounds when wet and capable of elongation without rupture by from 3 to 50% of its length whether wet or dry.

2. A disposable article or material according to Claim 1, wherein the fibres of both the fibrous pad and the covering are cellulosic.

3. A disposable article or material according to Claim 1 or 2, wherein 10 to 60% of the weight of the covering consists of the organic polymer.

4. A disposable article or material according to Claim 1, substantially as hereinbefore described.

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